Nuclear magnetic resonance (NMR) spectroscopy is a versatile tool for screening complex mixtures. In general, the spectrum of a mixture is the sum of the spectra of its components, so information for each component can be obtained from the spectrum without fractionation or purification. Components can be identified by comparison against a library of known compounds. The signal strength is linearly proportional to the amount of each component (and the number of nuclei contributing to each signal), so quantification of each component is readily available from the spectrum. Thus, composition of the mixture can be determined both qualitatively and quantitatively from a single NMR spectrum in full automation.

Commercial products such as detergents are good examples of complex mixtures. It is strategically important to examine competitors’ products, to identify new ingredients and changes to formulation. It is also essential to verify the composition at various stages of production. NMR spectroscopy is a useful tool for these applications, including quantitative analysis of the components.

In this report, we demonstrate some of the information available for commercial dishwashing liquid. Using 1D 1H NMR spectroscopy, we can identify controversial ingredients, search for advertised botanical ingredients, compare detergents marketed as hypoallergenic against the original formula, distinguish between major brands, and recognize similarities between a premium line and its bargain brand counterpart. We also note that this analysis can be extended to other home cleaning and personal care products.

**Materials and methods**

31 samples of hand dishwashing liquid detergent were examined by NMR spectroscopy. Samples were obtained at home, at work, and from stores including CVS (drugstore), Market Basket (grocery store), and Walmart (discount department store). For spectroscopy, 10 µL of detergent was diluted with 590 µL of 2H2O containing DSS as a chemical shift reference. Spectra were acquired with the Bruker noesygppr1d pulse sequence, which is a 1D NOESY spectrum with presaturation for water suppression. Spectra were recorded at 600 MHz on a Bruker Avance III spectrometer equipped with a 5 mm TCI CryoProbe. 32 scans were accumulated for an experiment time of 2 minutes, 15 seconds.

**Identifying the controversial antibacterial, triclosan**

Triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol, 1) is a widely used antibacterial found in dishwashing liquid, hand soaps, and body washes. Although there are no proven adverse health effects, as a chlorinated aromatic compound,
it is related to dioxin (2), it has been suggested that it can mimic steroid hormones, and it is known to accumulate in the environment†. Furthermore, soaps containing triclosan have not been shown to be significantly more effective as antibacterials than soap alone‡. Thus, triclosan is a controversial ingredient and is being phased out; legislation has been signed in Minnesota that bans it after January 1, 2017. Triclosan is readily detected and quantified in the 1D ¹H NMR spectra of dish detergents (Figure 1).

Reformulation of “hypoallergenic” products

Consumers are increasingly concerned about the ingredients in their household products. Many detergents offer “hypoallergenic” formulations that may eliminate unnecessary and potentially harmful chemicals added as dyes and fragrances, hence the proliferation of white bottles of laundry detergent and clear bottles of dishwashing liquids on store shelves. Dawn’s product that follows this trend is called “pure essentials”. It contains similar ingredients to “original scent,” including the fragrance (Figure 2A, with inset). However, Palmolive’s product, “pure+clear”, is completely reformulated, featuring different surfactants (Figure 2B).

**Figure 1**

1D ¹H spectra of different varieties of Dawn dishwashing liquid. The peaks due to triclosan appear for the antibacterial product (red spectrum with triclosan indicated by red arrows). The concentration was determined to be 2.1 mM, using Bruker’s Assure-RMS software with calibration to an external standard.

**Figure 2**

Comparing “hypoallergenic” versions of dishwashing liquid to the original formulations. (A) The ¹H NMR spectrum of Dawn pure essentials (in blue) is very similar to the ¹H spectrum of original scent (in black), even in the aromatic region of the spectrum where dyes and fragrances appear (inset). Multiplets at 3.65 and 1.17 ppm in the spectrum of original scent correspond to ethanol. (B) The ¹H NMR spectrum of Palmolive pure+clear (in green) shows that the detergent is significantly reformulated compared to Palmolive original (spectrum in black).

†http://www.epa.gov/oppsrrd1/REDs/factsheets/triclosan_fs.htm
‡http://www.fda.gov/ForConsumers/ConsumerUpdates/ucm205999.htm
Searching for botanical ingredients

Many manufacturers advertise added botanical ingredients in their detergents. However, few define how much of the “natural” ingredient is present. Comparison of the 1D $^1$H NMR spectrum of Palmolive with Aloe to a spectrum of Aloe vera powder suggests the actual concentration of Aloe vera in the dishwashing liquid is below our detection limit (hundred µM range), possibly too low to have much of the expected effect for the botanical (Figure 3).

So then what are you paying for?

The first ingredient on all the lists for dishwashing liquids is water; water can be 80% or more of the product by weight. Water can be observed directly by NMR (Figure 4). We can see by direct comparison of the water peaks in Palmolive Ultra original and Palmolive with orange extracts that the consumer who bought Palmolive with orange extracts got more water per volume.

A trend in cleaning products is to offer concentrated versions. In dishwashing liquid, these are typically designated “Ultra” and represent a two-fold concentration. Offering similar products at different strengths makes it more difficult for the consumer to compare the pricing. Differences in concentration are readily detected by NMR (Figure 5). Peak intensities are proportional to the amount of each component and directly reflect the concentration.
Component screening and quantification

The spectrum of a complex mixture such as a dishwashing liquid can be compared against reference spectra of likely components to identify the ingredients. In general, ingredients for dishwashing liquid are publicly disclosed online. Reference spectra can be simplified and stored in an NMR database (an SBASE) for convenient comparison against new samples. Comparison against a detergent SBASE confirmed some of the ingredients in Method dishwashing liquid, as seen in Figure 6.

Although the ingredients are disclosed, their proportions are proprietary. Peaks from different components can be integrated and the area compared against an external reference of known concentration to yield concentrations for each component. The concentrations of several compounds in Method dishwashing liquid are reported in the Table. The linefits are shown in Figure 7. The acquisition, processing, fitting and concentration calculations were done in automation using the Assure-RMS software (Bruker BioSpin).

Table: Concentration of selected components of Method dishwashing liquid, determined with Assure-RMS.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Function</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium lauryl sulfate</td>
<td>surfactant</td>
<td>246.47</td>
</tr>
<tr>
<td>ethanol</td>
<td>solvent</td>
<td>30.08</td>
</tr>
<tr>
<td>glycerol</td>
<td>solvent</td>
<td>66.92</td>
</tr>
<tr>
<td>citric acid</td>
<td>complexing agent</td>
<td>10.98</td>
</tr>
</tbody>
</table>

Identifying components in Method dishwashing liquid by comparison against an NMR reference spectral database (SBASE) generated in Assure-RMS.

Examples of fits for peaks chosen to quantitate compounds in the table above. Analysis, including line fitting, was done with the Assure-RMS software (Bruker BioSpin). The sample is Method dishwashing liquid.
Fast spectral comparisons using multivariate statistics for product intellectual property

With enough representative samples, multivariate statistics can be used to compare sets of spectra. Principal component analysis (PCA), implemented with the AMIX software (Bruker BioSpin), was used to compare the brands Dawn and Palmolive (Figure 8). Dawn and Palmolive can be distinguished by PCA based on principal component 1 (PC1). Based on the loadings plot (not shown), PC1 corresponds to the surfactants present in the dishwashing liquid. This analysis potentially provides the means to identify different surfactants, providing a monitoring tool for protecting intellectual property.

SIMCA model for classifying products: Dawn and Joy are in the same class

Since Dawn and Palmolive can be distinguished based on PCA of their 1D $^1$H spectra, we can build statistical models for each brand using soft independent modeling of class analogies (SIMCA), implemented in the Assure-RMS software (Bruker BioSpin). Then other brands can be tested against the models to determine whether these products fall in the same class. For example, store brands are often manufactured by the same companies that manufacture brand name products; SIMCA classification can be used to identify which company most likely produced the store brand. Here we test the brands Method and Joy against our Dawn SIMCA model. For Method dishwashing liquid, we demonstrate that Method is a distinct product (Figure 9). However, testing Joy, we see it fits within the Dawn SIMCA model (Figure 10). This is especially interesting because Dawn and Joy are both manufactured by Procter & Gamble. Perhaps the distinctly marketed brands provide needed market competition?
**Conclusions**

Using dishwashing liquid as an example, we have demonstrated several ways in which NMR spectroscopy can be used for composition analysis and competitive intelligence. These applications can be automated using the Assure-RMS software for data acquisition, analysis, and reporting, providing a fast and easy solution. Using component analysis, changes to the formulation can be detected. Specific ingredients can be identified and quantitated. Using multivariate statistical analysis, models for different classes of product can be developed and used to test unknown samples. With the sensitivity and stability of modern spectrometers, long-term monitoring of products by NMR is a powerful strategy for competitive intelligence.

**Beyond dishwashing liquid: Other household cleaners and personal care products**

Although we focused on hand dishwashing liquid, other household cleaning products contain similar ingredients. Figure 11 shows a spectrum of laundry detergent (Tide Free & Gentle). Some of the components can be identified using the reference spectral database developed for hand dishwashing liquid. Of special interest, we can identify citrate (Figure 11, inset), which is not among the ingredients listed online (http://www.pgproductsafety.com/productsafety/ingredients/household_care/laundry_fabric_care/Tide/Liquid_Tide_Free_Gentle.pdf).

Personal cleansing products such as hand soap, body wash, and shampoo are also suitable for scrutiny by NMR spectroscopy. We recorded 1D $^1$H spectra of several varieties of Softsoap (Figure 12). By comparing the 1D spectra, we immediately recognize that there are two different formulations of Softsoap, one exemplified by the aquarium series, crisp cucumber & melon, and pomegranate & mango; the other represented by soothing aloe vera and lavender & chamomile.

![Figure 11](image1.png)

**1D $^1$H spectrum of Tide Free & Gentle. Note citrate is clearly identified in the spectrum, based on the SBASE match (not shown) and fit (shown as an inset), performed with Assure-RMS. Citrate is not listed as an ingredient.**

![Figure 12](image2.png)

**Example of a personal care product: Softsoap. Based on the 1D $^1$H spectra, we can identify two different formulations of Softsoap, one represented by the aquarium series, crisp cucumber & melon, and pomegranate & mango (top three spectra, above), the other represented by soothing aloe vera and lavender & chamomile (bottom two spectra, above). The bottom two contain unsaturated (olefinic) chains in the surfactants, while the top three do not, as demonstrated by the presence of peaks from 7 to 5 ppm.**